Preliminary Results of Oil Fingerprint Evaluation of Soil, Water & Oil Samples Supplemental Information

Date: May 19, 2013
To: R. Singhvi, ERT Work Assignment Manager (WAM)
From: J. Syslo, SERAS Analytical Support Chemist
Through: D. Miller, SERAS Program Manager
Project: Guayanilla Bay Oil Spill: WA# SER03017
COC#: 002700175-4.29.2013-001, -002, -003, -004

A request was made to provide a more detailed fingerprint assessment of three soil samples (S-025-3033-001, S-026-1216-001 and S-022-2226-001) after issuing the preliminary results on May 16, 2013. This memo provides supplemental information and a revised assessment with greater detail for some of the samples. While reexamining the soil sample fingerprints, the fingerprints for the oil/product samples were also reexamined and some additional insight and information on those samples is also presented in this report.

Fingerprint Assessment of Soil Samples S-022-2226-001, S-025-3033-001 and S-026-1216-001:

The following samples & standards are used for this evaluation:

- Kerosene reference oil standard.
- OI-001-001: product from "Manhole" (M) location.
- SD-002-006-001: soil extract from "Discharge point" (DP) location.
- S-014-1216-002: soil extract that I believe to be fingerprint of another product that was mixed with the kerosene product when it contacted the environment. Note, I will refer to this as S-014 but this isn't to be confused with S-014-1216-001, which contains a slightly different fingerprint.
- S-022-2226-001: soil extract that shows a mixture of product or product mixture identified in 3/22 samples plus and additional product labeled as "waxy product".
- S-025-3033-001: soil extract that contains mostly gasoline and elements of S-014, and the "waxy product".
- S-026-1216-001: soil extract that contains mostly gasoline and elements of S-014, and the "waxy product".

Although it was difficult to separate, classify, and identify the different products observed in the samples, I have arrived at the following conclusions based upon a thorough evaluation or many different fingerprints:

1. The fingerprints of "Manhole" (M) and "Discharge Point" (DP) contained a mixture of a slightly biodegraded light product labeled as kerosene with another oil biodegraded light #2 oil. The fingerprint evidence show that the biodegraded #2 oil has mixed with a kerosene type light oil, and there are different mixtures ratios present, or observed in different samples. There is no example of a 'pure" uncontaminated kerosene product, but the two M samples of 3/22 contain mostly slightly biodegraded form of the kerosene. The fingerprints of the two DP samples are mixture of the kerosene product with the "other" degraded oil too, but the kerosene has undergone a greater level of evaporative weathering. These were the only two products observed in the 3/22 samples. **Figure A** shows fingerprints that focus on the lighter alkyl-benzene fraction compared to the TPH-alkanes (ion 85 + 83) fraction for those samples.
2. **Figure B** shows the ion 183 fingerprints of kerosene, M, DP, S-003, S-014 and S-022. The ion 183 fingerprint is very useful to determine if kerosene is mixed with a heavier oil such as #2 oil or heavier. These six fingerprints show how the 183 fingerprint is altered due to the addition of the biodegraded #2 oil. The difference between the M and DP fingerprint is due to the loss of lighter compounds from simple evaporation and the #2 ion 183 contribution (hump between 16 to 24 minutes)is more apparent. Sample S-003 is illustrated because it was the closest match to the M sample from the recent batch of samples. The fingerprint of soil sample S-014 is what I believe to be derived from *just the "other"* biodegraded #2 source. Given the time & resources, I could mix extracts or product of kerosene at the correct ratio to product the ion 183 fingerprints of M or P. The fingerprint of S-022 is *very similar* the fingerprint of DP. This is the first piece of evidence that alludes to S-022 does contain some of the product(s) identified in the 3/22 samples.

3. **Figure C** shows stacked fingerprints of 113/183/193 which use isoprenoids and other biodegradation resistant compounds to evaluate product mixing and matching. The 113 fingerprint represents both alkanes and isoprenoids and it can be clearly seen that the M & DP samples retain the isoprenoids, but have had the alkanes removed from early stages of biodegradation. It can also be observed that the biodegradation occurred before evaporative weathering when comparing kerosene to the M sample. When comparing M to DP, the ion 113 fingerprint changes du to the evaporative loss of the earlier/lighter isoprenoids and the addition the heavier isoprenoids due to mixing with the weathered #2 oil. Sample S-014 represents an isolated example of the weathered #2 oil. When comparing S-014 with the DP sample, one can also observe the 183/193 fingerprints, where the total pattern and ratio (the fingerprints are not normalized) of 183 to 193 are similar. The total 113/183/193 fingerprint of S-022 resembles that of DP, except S-022 has a higher concentration of lighter compounds, which have been stripped from the DP sample from evaporative weathering. This is another piece of evidence that shows that sample S-022 may contain some of the 3/22 product(s). The 113/183/193 fingerprints of S-025 and S-026 match each other, and show that S-022 is most likely a slightly biodegraded version of S-025 and S-026.
4. **Figure D** illustrates the ion 123 fingerprint that highlight very bio-resistant compounds such as bicyclic sesquiterpanes. The kerosene & M fingerprint are similar except for the slight contribution of the degraded #2 hump. The DP fingerprint shows further alteration due to addition of more of the degraded #2 oil. The sample S-014 fingerprint is probably all from the degraded #2 oil. Both pure kerosene and the degraded #2 oil produce ion 123 "humps" that have occur in different regions of the GC/MS chromatogram. When the two oils are mixed, one can observe two distinct humps, as in the DP sample. The S-022 ion 123 fingerprint is very similar and almost identical to the DP sample, and another strong piece of evidence that show that S-022 does contain the product(s) identified in sample DP. The fingerprints of S-025 and S-026 match each other and are a very good match to S-022. The ion 123 pattern of the S-025 and S-026 samples indicate that there is a high degree of product mixing. With this level of mixing, it is difficult to determine, but not rule out the possibility that the products observed in the 3/22 samples are present. But, the oil in S-025 and S-026 are *not* the spilled product contained in the M or DP samples, but may contain some of that product.
5. **Figure E** shows the total ion chromatograms (TIC) for kerosene, M, DP, S-014, S-022, S-025 and S-026. Using the TIC, it is difficult to observe conclusive matches for all these samples, yet some similarities are apparent. The TIC fingerprints are similar to what a GC/FID fingerprint would produce, and it is nearly impossible to identify and differentiate separate products when there are mixtures. What can be observed with this "broad and general" fingerprint is:
    a. That the TIC for kerosene is similar to M
    b. The TIC for the DP sample is composed of a mixture of the fingerprints from M and S-014.
    c. The TIC for samples S-025 and S-026 indicate that there is an oil mixture unlike the M or DP samples, that has a high concentration of gasoline compared to the other "stuff" in that oil. Sample S-025 has a higher gasoline concentration than S-026
    d. Sample S-022 shows the fingerprint of a medium range distillate oil that does not exactly match the M or DP samples, although other fingerprint evidence show that there is a very good possibility that there is a match to the DP oil. The TIC fingerprint for the product observed in S-022 is unlike the M or DP fingerprints, but most likely masks any presence of M or DP products. The TIC in S-022 can be matched to the TIC's of S-026 and S-025. The observed differences in the TIC's for these three soil extracts are due to the amount of gasoline present, which drives the fingerprint scale for the TIC. Sample S-025 contains the most gasoline, followed by S-026, and S-022 containing the least amount.

Additional Fingerprint Assessment of the Six Oil Samples:

Examination of the six oil/product samples provides additional information to the nature and identity of the oil observed in the three soils requested and all the samples combined.

1. **Figure F** shows the ion 123 fingerprints for CO009, CO012, CO023, SH101, SH102 and SH303, and indicates that there is a mixture of products, or a product that is composed of a mixture of different elements. The total ion 123 fingerprint show that samples CO009, CO012 and SH102 match each other and samples CO023 and SH303 match each other. Sample SH101 appears to be a mixture that is a match to both groups of samples. All six products contain the same elements, just at different ratios, or mixtures. The ion 183/193 stacked

fingerprints of **Figure G** support that there is a match for all the oil/product samples. Samples grouped as (CO009, CO012, SH102) and (CO023, SH101, SH303) are exact matches to each other. There is a slight difference in the patterns of the two groups is due to contribution of another, possibly unknown product.

2. **Figure H** shows the ion 183 fingerprints for all six oil/product samples. All six show the pattern of n-saturated alkanes eluting at the tail end of the chromatogram between 19 to 30 minutes, which indicate they all have the "waxy distillate" in common. All six fingerprints are almost identical matches, except for a greater abundance of lighter compounds SH101, and to a lesser degree in CO023 and SH303.
3. **Figure I** compares the ion 183 fingerprints of a bio-weathered #2 fuel oil , SH101, SH102, S-022, S-025 and S-026. These fingerprints show that S-025 and S-026 contain the same product/product mixture identified in all of the oil/product samples. The "waxy distillate" present in all the oils as well as S-025 & S-026 is also observed in S-022, but S-022 contains less of this "waxy" product.

Revised Final Assessment &Conclusion:

This is a revised assessment based upon the examination of many new extracted fingerprints that were not thoroughly examined and taken into consideration with the release of the 5/16/13 preliminary results. There are many factors that had to be considered and weighed such as the mixture of different products, different degrees of both evaporative and biodegradative weathering, changes in fingerprints due to contact with the environment, and the amount of time the product was in contact with the environment after release. The fingerprint assessment becomes even more difficult without a actual, fresh, known source to compare the samples with.

I will present this assessment as a chronology which is based on actual fingerprint evidence and some speculative insight based upon my experience of examining ad assessing oil fingerprint data for 25 years. **Figure J** presents ion 123 fingerprints to provide the illustrate various aspects of how I arrived at my conclusions. The samples labeled "manhole" and "discharge point" received on 3/22/13 were identified as a mixture of at least two different products. It is speculated that there was a release of a product resembling and identified as kerosene (1).

The 3/22 product "manhole" (2) is a slightly biodegraded form of kerosene, but has picked up some heavier non-kerosene product when the spilled oil came into contact with the environment. The oil identified in S-014-1216-002 (3) is most likely representative of the heavier "non-kerosene" product that was picked up or mixed by the kerosene. The 3/22 sample collected at "discharge point" (4) contains elements of both the "manhole" product and the S-014 oil. The "manhole" product has undergone extensive evaporative weathering of most of the more volatile "light" compounds, and the resulting oil mixture fingerprint shows there is a mixture of "manhole" product with the degraded #2 oil, and possibly another product that has probably undergone extensive biodegradation. The source and identity of the 3rd product (see fingerprint (4)) has not been determined and may possibly be linked to an old background spill that covers a large area.

The ion 123 fingerprint of soil sample S-022 (5) shows a strong correlation to the fingerprint of the "discharge point" sample. Combined with other evidence, the ion 123 indicates that S-022 may contains the same oil mixture identified in "discharge point". In addition to the DP oil, a different, possibly unrelated fresh product has been identified in this sample.

Soil samples S-025 and S-026 contains a product that is unlike the "manhole" product, yet may contain some of the "discharge point" product. The ion 123 fingerprints of S-025 (6) and S-026 (7) match each other and are a strong match to S-022. Other fingerprints indicate that S-022, S-025 and S-026 contain a large amount of gasoline compared to the other identified products. There appears to be a gasoline product mixed with a refined oil referred to as the "waxy distillate" in other segments of this and the 5/16 prelims.

The ion 123 fingerprints of product/oil samples CO009(8), CO012(9) and SH102(10) all match each other. There is also a very strong overall fingerprint match to soil samples S-025, S-026 and to a lesser extent, S-022. Samples S-025 and S-026 appear to contain less of the unknown "lighter fraction" of compounds that make up the fingerprint from 4 to 12 minutes. This is not due to depletion of gasoline compounds or biodegradation. The three oil/product samples contain something else that is not present in S-025 & S-026.

Oil/product samples CO023(11) and SH303(12) contain a higher ratio of the unknown "lighter fraction" observed in oil samples CO009(8), CO012(9) and SH102(10). CO023 and SH303 match each other.

Oil/product sample SH101(13) contains the highest amount of the unknown "lighter fraction" when compared to the product mixtures of all the other oil samples. Based upon observing an abundance of the n-methyl-cyclohexane peaks The unknown "lighter fraction" appears to vary in concentration relative to a uniform product mixture that is common to all the oil/product samples.

All the oil/product samples contain a similar BTEX to alkyl-benzene ratio that is comparable to gasoline. The slight differences between the BTEX and total alkyl-benzene ratio appear to be due to an evaporative loss of the BTEX compounds. Since the oil/product samples were processed by a similar waste dilution method, the total alkyl benzene concentration appears to be fixed within the product mixture while the concentration of BTEX varies.

Figure K presents ion 85 and ion 83 fingerprints, and resulting chromatograms show individual saturated n-alkane peaks for ion 85 and the individual n-methyl-cyclohexane peaks for ion 83. A gasoline and kerosene standard are provided with the saturated n-alkanes labeled in the ion 85 fingerprints. The ion 85 fingerprint of the gasoline standard show the pattern of n-alkanes from octane through tetradecane. The ion 85 fingerprint for kerosene show the pattern of n-alkanes from octane (C8) through nonadecane (C19). The ion 85 fingerprints for all the oil/product samples show a pattern that matches the gasoline standard, except SH101. The n-alkane pattern that extends beyond the C14 range is not from gasoline, but from the "waxy distillate".

The "waxy distillate" may be a uniform light to middle refined distillate from a heavier petroleum product with an abundance of compounds that cover the gasoline range organics (GRO) to the diesel range organics (DRO). The ion 85 and ion 83 patterns indicate that there is no significant signs of biodegradation, and only a slight degree of evaporative weathering. Based on these observations, if these product samples were collected from the environment, then these samples have not been in contact with the environment very long and represent a relatively fresh spill.

Finally, the difference in the ion 85 and ion 83 fingerprints of SH101 and all the other product samples and gasoline standard may be caused by the presence of a relatively "fresh" light oil similar to kerosene. This statement shouldn't be misconstrued as a correlation to the product or product mixture of the 3/22 samples. All of the fingerprint evidence used to assess and identify the product mixture of the six oil samples of 5/7 indicate that there is a uniform mixture of a wide range of petroleum compounds. Besides the uniform light to middle distillate common to all the oil/product samples, sample SH101 appears to contain another separate "light product" comparable to kerosene.

As I stated earlier, this task was not easy without having a potential source oil to compare to the samples. Things became complicated because I had some 5/07 samples match and correlate with the 3/22 samples, and others that appeared to be something totally different. Upon this closer examination, I did detect some hidden correlative fingerprints which indicate that there is a different fresh oil spilled & mixed with the oil detected in the 3/22 samples. I can't ascertain whether the fresh light product that has been detected in SH101 is in any way linked or related to what was identified in the "manhole" and "discharge point" samples. The fingerprints inherit to the uniform "waxy product" combined with the fingerprints related to the weathered #2 oil obscure and prevent a clear distinction for a positive match.

If you have any further questions or inquiries, please don't hesitate to contact me. I hope this report was sufficient to clarify and expand upon some of the general conclusions of the 5/16 results. All the figures are attached as .pdf files which should be opened and printed to support this report. It was easier to organize the presentation of fingerprints using individual .pdf files rather than scan in the results/text followed by all the fingerprints.

J Syslo 05/19/13